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## PATENT COOPERATION TREATY

PCT

## NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Commissioner  
US Department of Commerce  
United States Patent and Trademark  
Office, PCT  
2011 South Clark Place Room  
CP2/5C24  
Arlington, VA 22202  
ETATS-UNIS D'AMERIQUE  
in its capacity as elected Office

Date of mailing: 11 January 2001 (11.01.01)	
International application No.: PCT/ZA00/00120	Applicant's or agent's file reference: PC/ZA00/F221
International filing date: 06 July 2000 (06.07.00)	Priority date: 06 July 1999 (06.07.99)
Applicant: BOTHA, Jan, Mattheus et al	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International preliminary Examining Authority on:

04 October 2000 (04.10.00)

☐ in a notice effecting later election filed with the International Bureau on:2. The election ☒ was☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35	Authorized officer:  J. Zahra Telephone No.: (41-22) 338.83.38
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# PATENT COOPERATION TREATY

# PCT

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference <b>PC/ZA00/F221</b>	<b>FOR FURTHER ACTION</b> see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. <b>PCT/ZA 00/ 00120</b>	International filing date (day/month/year) <b>06/07/2000</b>	(Earliest) Priority Date (day/month/year) <b>06/07/1999</b>
Applicant  <b>SASOL TECHNOLOGY (PTY) LTD</b>		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

**1. Basis of the report**

a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

☐ contained in the international application in written form.

☐ filed together with the international application in computer readable form.

☐ furnished subsequently to this Authority in written form.

☐ furnished subsequently to this Authority in computer readable form.

☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,

☒ the text is approved as submitted by the applicant.

☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

☒ as suggested by the applicant.

☐ because the applicant failed to suggest a figure.

☐ because this figure better characterizes the invention.

1  
☐ None of the figures.

## INTERNATIONAL SEARCH REPORT

International Application No

ZA 00/00120

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07C6/04

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	R. L. BANKS: "Catalytic Olefin Disproportionation" FORTSCHRITTE DER CHEMISCHEN FORSCHUNG - TOPICS IN CURRENT CHEMISTRY, vol. 25, 1972, pages 40-69, XP000953147 Berlin table 1	1-34
X	EP 0 538 750 A (MARUZEN PETROCHEMICAL CO) 28 April 1993 (1993-04-28) claims	1-34
X	EP 0 056 013 A (BP CHEMICALS ) 14 July 1982 (1982-07-14) claims	1-34
	--- -/--	



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

## \* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*Z\* document member of the same patent family

Date of the actual completion of the international search

26 October 2000

Date of mailing of the international search report

07/11/2000

Name and mailing address of the ISA

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Authorized officer

Van Geyt, J

## INTERNATIONAL SEARCH REPORT

International Application No

/ZA 00/00120

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	WO 00 14038 A (BOTHJA JAN ET AL) 16 March 2000 (2000-03-16) claims -----	1-34

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No


ZA 00/00120

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
EP 0538750	A	28-04-1993	JP	5103995 A	27-04-1993
			CA	2080770 A	18-04-1993
			DE	69204796 D	19-10-1995
			DE	69204796 T	22-02-1996
			US	5304692 A	19-04-1994
EP 0056013	A	14-07-1982	DE	56013 T	28-04-1983
			JP	58126818 A	28-07-1983
			US	4368345 A	11-01-1983
WO 0014038	A	16-03-2000	AU	4925799 A	27-03-2000

# PCT

## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference PCT/ZA00/00120		<b>FOR FURTHER ACTION</b>	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/ZA00/00120	International filing date (day/month/year) 06/07/2000	Priority date (day/month/year) 06/07/1999	
International Patent Classification (IPC) or national classification and IPC C07C6/04			
Applicant SASOL TECHNOLOGY (PTY) LTD. et al.			
<p>1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 5 sheets, including this cover sheet.</p> <p><input type="checkbox"/> This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).</p> <p>These annexes consist of a total of sheets.</p>			
<p>3. This report contains indications relating to the following items:</p> <ul style="list-style-type: none"> <li>I <input checked="" type="checkbox"/> Basis of the report</li> <li>II <input type="checkbox"/> Priority</li> <li>III <input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</li> <li>IV <input type="checkbox"/> Lack of unity of invention</li> <li>V <input checked="" type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</li> <li>VI <input checked="" type="checkbox"/> Certain documents cited</li> <li>VII <input type="checkbox"/> Certain defects in the international application</li> <li>VIII <input checked="" type="checkbox"/> Certain observations on the international application</li> </ul>			
Date of submission of the demand  04/10/2000		Date of completion of this report  07.08.2001	
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465		Authorized officer  Pfannerer, F  Telephone No. +49 89 2399 8322	



**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/ZA00/00120

**I. Basis of the report**

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

**Description, pages:**

1-11 as originally filed

**Claims, No.:**

1-34 as originally filed

**Drawings, sheets:**

1/1 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:



**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/ZA00/00120

☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

*(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)*

6. Additional observations, if necessary:

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

**1. Statement**

Novelty (N)	Yes: Claims	
	No: Claims	1-11
Inventive step (IS)	Yes: Claims	
	No: Claims	1-34
Industrial applicability (IA)	Yes: Claims	1-34
	No: Claims	

2. Citations and explanations  
**see separate sheet**

**VI. Certain documents cited**

1. Certain published documents (Rule 70.10)

and / or

2. Non-written disclosures (Rule 70.9)

**see separate sheet**

**VIII. Certain observations on the international application**

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:  
**see separate sheet**

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

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International application No. PCT/ZA00/00120

D1 = Fortschritte der Chem. Forschung - Topics in Current Chemistry  
vol.25 (1972) pages 40-69

D2 = EP-A-538 750

D3 = EP-A- 56 013

To section V

1. The process as defined in present claims 1 to 11 is anticipated by D1.  
Therefore, the subject-matter of said claims does not fulfil the requirements of Article 33(2) PCT.
2. In addition, having regard to the cited prior art cited and to the background, mentioned on pages 1 and 2 of the present description, the presently claimed subject-matter, when novel over D1, is regarded as being obvious to a skilled person.

To section VI

Reference is made to WO-A-00/14038, published on 16.3.00, claiming the priority right of 4.9.98.

To section VIII

- (a) Terms such as "high" temperature and "metathesis conditions" are indefinite and therefore unclear and should be replaced by the temperatures and conditions actually used. (reference is made to Article 6 PCT)
- (b) Present claims 9-11,20,23-26 are defined by the desired result of the process. The claims should be replaced by claims which define the measures necessary for achieving a desired result or should be deleted. (see Art. 6 and Rule 6.3 (b) (ii) PCT)
- (c) Present claim 15 is largely repetitive of claim 1 and should therefore be rendered

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

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International application No. PCT/ZA00/00120

dependent on claim 1 only defining the additional feature or features. (see Rule 6.4 PCT)

- (d) Present claims 17,18,30-32 relate to repetitions of foregoing claims and should therefore be deleted. (see Rule 6.1 PCT)
- (e) With respect to present claims 33 and 34 reference is made to Rule 6.2 (a) PCT.

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
11 January 2001 (11.01.2001)

PCT

(10) International Publication Number  
**WO 01/02324 A1**

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(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
60/142,382 6 July 1999 (06.07.1999) US  
99/04380 6 July 1999 (06.07.1999) ZA

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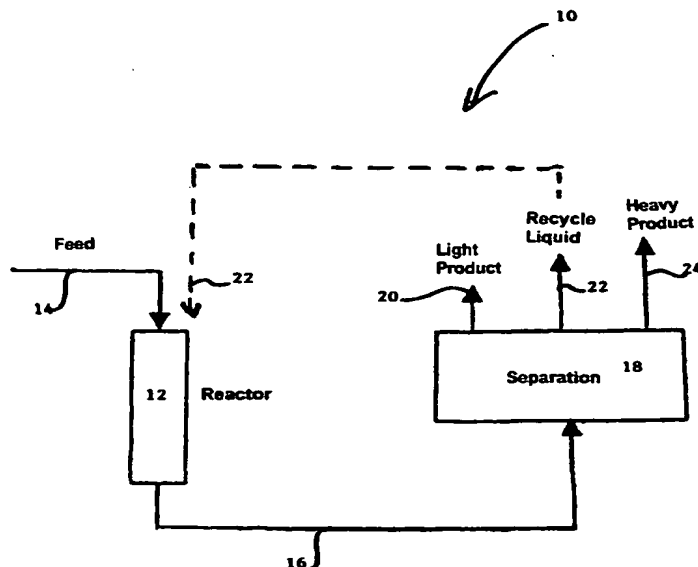
(74) Agent: DUNLOP, Alan, J., S.; Hahn & Hahn Inc., 222 Richard Street, Hatfield, 0083 Pretoria (ZA).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, FR, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian

[Continued on next page]

(54) Title: HIGH TEMPERATURE METATHESIS PROCESS



(57) Abstract: The invention provides a high temperature metathesis process for the metathesis of Fischer-Tropsch olefins in the C<sub>5</sub> to C<sub>15</sub> range, said metathesis process including the step of subjecting a Fischer-Tropsch olefin feedstock in the C<sub>5</sub> to C<sub>15</sub> range to metathesis reaction conditions, said olefin feedstock including mono-methyl branched olefins. The invention also provides alkyl benzenes (AB's), drilling fluids and oxo-alcohols produced from the products of the metathesis process.



patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

**Published:**

— With international search report.

— Before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments.

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

## HIGH TEMPERATURE METATHESIS PROCESS

### Field of the Invention

5        This invention relates to a high temperature metathesis process. In particular, the invention relates to the optimisation of the high temperature metathesis process to improve selectivity for a desired product range.

### Background to the Invention

10

The applicant is aware that olefins in the C<sub>9</sub> to C<sub>14</sub> range may be used as detergent and plasticizer precursors as well as for alkylation of benzene, and that C<sub>15</sub> to C<sub>18</sub> olefin ranges may be used as drilling fluids and drilling fluid precursors, amongst other uses.

15

Conventional thinking was that linear olefins may be used to produce linear alkyl benzene and linear oxo-alcohols which could be used to produce detergents and plasticizers which were believed to be both bio-degradable and suitable for their intended purpose. Thus, previously efforts were concentrated on producing linear oxo-alcohols and lineal alkyl benzene, and thus efforts were focused on linear olefins from which these could be made.

20

Recently, however, a new wave of thinking has lead to the belief that non-linear oxo-alcohols as well as non-linear alkyl chain alkyl benzene could be used alone or together with their linear counterparts for the production of

25

said detergents and plasticizers. In particular short chain branched olefins are believed best suited to produce such non-linear products. Thus, recent efforts have concentrated on the delinearization of the linear olefins in order to use such olefins in the production of the non-linear products.

5

### Summary of the Invention

Surprisingly, after extensive research, the applicant has found that a peculiar olefin composition in the C<sub>9</sub> to C<sub>18</sub> range, having both linear and non-linear olefins may be made by metathesis of Fischer-Tropsch olefins in the C<sub>5</sub> to C<sub>15</sub> range.

Thus, according to a first aspect of the invention, there is provided a high temperature metathesis process for the metathesis of Fischer-Tropsch olefins in the C<sub>5</sub> to C<sub>15</sub> range, said metathesis process including the step of subjecting a Fischer-Tropsch olefin feedstock in the C<sub>5</sub> to C<sub>15</sub> range to metathesis reaction conditions, said olefin feedstock including mono-methyl branched olefins.

The high temperature metathesis process may be carried out at a temperature of between 300°C to 600°C.

Typically the high temperature metathesis process is carried out at a temperature of between 450°C and 550°C.

25

The operating pressure of the high temperature metathesis process may be between 1 and 30 bar, or even higher.

5 The high temperature metathesis process may use a tungsten or molybdenum based catalyst, for example,  $\text{WO}_3$  or  $\text{MoO}_3$ , supported or unsupported, with or without co-catalysts. The support can typically be  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$ ,  $\text{TiO}_2$ , or mixtures thereof.

10 The high temperature metathesis process Fischer-Tropsch olefinic feedstock in the  $\text{C}_5$  to  $\text{C}_{15}$  range may include linear alpha olefins, mono-methyl branched olefins, paraffins, dienes, aromatics, and the like.

Typically, the Fischer-Tropsch olefinic feedstock includes one or more olefins selected from the  $\text{C}_5$  to  $\text{C}_9$  range.

15

The product of the high temperature metathesis process may include one or more mono-methyl branched olefins in the  $\text{C}_9$  to  $\text{C}_{18}$  range.

20 The product of the high temperature metathesis process may include one or more linear olefins in the  $\text{C}_9$  to  $\text{C}_{18}$  range.

The product of the high temperature metathesis process may include one or more mono-methyl branched olefins and one or more linear olefins in the  $\text{C}_9$  to  $\text{C}_{18}$  range. The olefins of the product may be internal olefins.

25



The product of the high temperature metathesis process may be used in the production of alkyl benzene, plasticizers, detergents, drilling fluids, and the like, having both a linear fraction and a branched fraction (for alkyl benzene the alkyl chain is branched or linear).

5

Typically, the branched fraction will be mono-methyl branched. However, the branching may be di-methyl and/or ethyl.

According to a second aspect of the invention, there is provided a high  
10 temperature metathesis process for the metathesis of olefins in the C<sub>5</sub> to C<sub>15</sub> range, said metathesis process including the step of subjecting an olefinic feedstock in the C<sub>5</sub> to C<sub>15</sub> range to metathesis reaction conditions, the process including the recycling of a part of the product of the metathesis reaction to the reaction to increase the selectivity for a desired product range.

15

The olefinic feedstock may be a Fischer-Tropsch olefinic feedstock including mono-methyl branched olefins.

Typically, the olefinic feedstock includes one or more olefins in the C<sub>5</sub>  
20 to C<sub>9</sub> range.

Where the desired product range includes olefins in the C<sub>9</sub> to C<sub>18</sub> range, the process includes a separation stage wherein a recycle fraction in the C<sub>5</sub> to C<sub>8</sub> range is separated from the product and recycled to the reaction.

25

The quantity of recycle in the feedstock may be selected to provide a C<sub>9</sub> and higher selectivity of above 50%.

Generally, the quantity of recycle in the feedstock is selected to provide  
5 a C<sub>9</sub> and higher selectivity of above 50%.

Typically, the recycle makes up between 20% and 80% of the reaction feedstock.

10 Usually, the recycle makes up between about a third and three quarters of the reaction feedstock.

The total yield of high temperature metathesis process product in the C<sub>9</sub> to C<sub>18</sub> range is above 40%.

15

Typically, the total yield of high temperature metathesis process product in the C<sub>9</sub> to C<sub>18</sub> range is about 50%.

The total feedstock conversion of the high temperature metathesis  
20 process of the invention is typically in the range of 60% to 90%, usually about 80%.

The ratio of linear to branched high temperature metathesis process products is typically greater than 1:1.

25

Usually, the ratio of linear to branched high temperature metathesis process products is greater than 2:1.

Generally, the ratio of linear to branched high temperature metathesis  
5 process products is about 3:1.

The branching of the high temperature metathesis process products is predominantly mono-methyl branching, although some di-methyl, and/or ethyl branching may also be present.

10

The product of the high temperature metathesis process may be used in the production of alkyl benzene, plasticizers, detergents, drilling fluids, and the like, having both a linear fraction and a branched fraction (for alkyl benzene the alkyl chain is branched or linear), the ratio of linear to branched  
15 fractions being related to the ratio of linear to branched high temperature metathesis process products used in their production.

### **Description of the Drawing and Examples**

20 The invention will now be described, by way of non-limiting illustration only, with reference to the accompanying line diagram.

In the diagram, reference numeral 10 generally indicates a high temperature metathesis process broadly in accordance with the invention.

25

The process 10 includes a reactor 12 operated at between 450°C and 550°C and at an operating pressure of between 1 and 30 bar. A Fischer-Tropsch olefinic feedstock 14 including mono-methyl branched olefins, is fed into the reactor 12. The feedstock 14 includes olefins in the C<sub>5</sub> to C<sub>9</sub> range.

5

Usually the feedstock 14 will be purified of oxygenates which may poison the catalyst by extractive distillation (not shown), prior to being fed to the reactor 12.

10 The reaction product 16 includes both linear and branched internal olefins in the C<sub>2</sub> to C<sub>18</sub> range.

The reaction product 16 is fed to a separator 18 where it is cut into a light product stream 20 including C<sub>2</sub> to C<sub>4</sub>, a recycle stream 22 including C<sub>5</sub> to  
15 C<sub>8</sub>, and a heavy product 24 including product in the desired C<sub>9</sub> to C<sub>18</sub> range.

The recycle stream 22 is combined with the feedstock 14 to form the total feedstock of the reactor 12.

20 The recycle stream 22 is between a third and three quarters of the feedstock 14.

The total yield of heavy product stream 24 is about 50%, while the feedstream 14 conversion is about 80%, with a selectivity for C<sub>9</sub> to C<sub>18</sub> of  
25 about 60%.

The ratio of linear to branched product in heavy product stream 24 is about 3:1

## 5        **Examples**

Several runs were made by passing olefin containing feed downwards through a vertical pipe reactor, unless otherwise stated. This reactor (25.4 mm in diameter and 400 mm in length) was positioned in a temperature-  
10    controlled electric furnace with a thermocouple positioned in the catalyst bed to monitor reaction temperatures.

About 100 mm depth of glass beads (2 mm diameter) were placed at the bottom of the pipe reactor supported by a layer of quartz wool. Another  
15    layer of quartz wool was placed on top of the glass beads as support for the catalyst bed comprising of about 12 g of catalyst. This was topped with another layer of quartz wool and the remainder of the reactor filled with glass beads. The catalyst was activated by heating at 550°C in flowing air for 12 hours, followed by heating at 600°C for 2 hours under a flow of nitrogen and  
20    finally the catalyst was cooled under a flow of nitrogen to reaction temperature (typically 500°C).

### **Example 1**

25        In this Example a catalyst in the form of a  $\text{WO}_3$  supported on  $\text{SiO}_2$  was used, in which the  $\text{WO}_3$  and  $\text{SiO}_2$  were in a mass ratio of 8:92. The process

was operated in the temperature range of 400 to 550°C and at a LHSV of 1 h<sup>-1</sup>

1. As a feed was used a C<sub>7</sub> SLO narrow cut after NMP extraction, containing 3-methyl-1-hexene (0.7870%), 5-methyl-1-hexene (1.9068%), 4-methyl-1-hexene (3.1737%), 2-methyl-1-hexene (4.1847%), 2-methylhexane (1.6501%), 3-methylhexane (2.8000%), 1-heptene (74.5710%), n-heptane (6.3012%), 2-methyl-2-hexene (0.6832%), 3-heptene (0.3163%), 2-heptene (0.7038%) and dienes, cyclic olefins and aromatics (2.4386%) amongst others, based on mass% calculations. Results are set forth in the following table, Table 1:

**Table 1**

Temp °C	400	450	475	500	525	550
C <sub>7</sub> Conversion (%)	4.4	20.4	50.0	65.9	71.9	78.4
Yield C <sub>9</sub> – C <sub>14</sub> (%)	2.4	8.9	20.3	23.9	20.2	13.9
Selectivity C <sub>9</sub> – C <sub>14</sub> (%)	55.6	43.9	40.6	36.3	28.1	17.7
Selectivity C <sub>2</sub>	0.4	0.3	0.3	0.7	1.2	2.7
Selectivity C <sub>3</sub>	5.0	2.6	2.7	4.6	7.7	14.0

## Example 2

In this Example a catalyst in form of a WO<sub>3</sub> supported on SiO<sub>2</sub> was used, in which the WO<sub>3</sub> and SiO<sub>2</sub> were in a mass ratio of 8:92. The process was operated at 500°C and by recycling some of the olefins formed back to the reactor. As a feed was used a C<sub>7</sub> SLO narrow cut after NMP extraction, containing 3-methyl-1-hexene (0.7870%), 5-methyl-1-hexene (1.9068%), 4-methyl-1-hexene (3.1737%), 2-methyl-1-hexene (4.1847%), 2-methylhexane

(1.6501%), 3-methylhexane (2.8000%), 1-heptene (74.5710%), n-heptane (6.3012%), 2-methyl-2-hexene (0.3163%), 2-heptene (0.7038%) and dienes, cyclic olefins and aromatics (2.4386%) amongst others, based on mass% calculations. Results are set forth in the following table, Table 2:

5

**Table 2**

Run	Feed Conversion (%)	C <sub>8</sub> Yield (%)	C <sub>9</sub> – C <sub>10</sub> Yield (%)	C <sub>11</sub> – C <sub>14</sub> Yield (%)	C <sub>15</sub> – C <sub>18</sub> Yield (%)	C <sub>8</sub> – C <sub>14</sub> Yield (%)
1 <sup>a</sup>	89.7	4.8	7.0	36.5	4.0	48.3
2 <sup>b</sup>	96.4	2.1	22.1	33.5	5.5	57.7
3 <sup>c</sup>	90.6	4.6	33.0	27.1	0.5	64.7
4 <sup>d</sup>	90.1	11.8	31.3	22.8	0.2	65.9

- (a) 1.0 LHSV based on fresh feed; 6.0 LHSV with recycle (1:5 recycle ration);  
 10 (Recycle C<sub>5</sub> – C<sub>10</sub>)
- (b) 1.4 LHSV based on fresh feed; 5.6 LHSV with recycle (1:3 recycle ratio);  
 (Recycle C<sub>5</sub> – C<sub>9</sub>)
- (c) 1.4 LHSV based on fresh feed; 5.6 LHSV with recycle 1:3 recycle ratio;  
 (Recycle C<sub>5/6</sub> – C<sub>8</sub>)
- 15 (d) 2.0 LHSV based on fresh feed; 5.0 LHSV with recycle 1:1.5 recycle ratio);  
 Recycle C<sub>4/5</sub> – C<sub>7</sub>)

### Example 3

20 In this Example a catalyst in the form of a WO<sub>3</sub> supported on SiO<sub>2</sub> were in a mass ratio of 8:92. The process was operated at 500°C and at a LHSV of 3 h<sup>-1</sup>. As a feed was used a C<sub>5</sub> SLO co-monomer grade cut containing 99% 1-pentene. The C<sub>5</sub> – C<sub>7</sub> fraction was recycled (1:1 recycle ratio) back to the

reactor in order to increase the yield towards the C<sub>8</sub> – C<sub>14</sub> fraction. Results are set forth in the following table, Table 3:

**Table 3**

<b>Temp °C</b>	<b>500</b>
<b>C<sub>5</sub> Conversion (%)</b>	<b>88.2</b>
<b>Yield C<sub>9</sub> – C<sub>14</sub> (%)</b>	<b>19.9</b>
<b>Selectivity C<sub>9</sub> – C<sub>14</sub> (%)</b>	<b>22.6</b>
<b>Selectivity C<sub>2</sub></b>	<b>5.2</b>
<b>Selectivity C<sub>3</sub></b>	<b>19.4</b>

5  
The applicant believes that it is an advantage of the invention as illustrated, that the high operating temperatures result in a high degree of  
10 resistance to poisoning of the metathesis catalyst by feedstock components, such as branched olefins, dienes, aromatics, and the like.

The applicant believes that it is a further advantage of the invention as illustrated that by recycling a cut of the product which is below the desirable  
15 carbon length range, high selectivity to desired products is achieved..



## Claims:

1. A high temperature metathesis process for the metathesis of Fischer-Tropsch olefins in the C<sub>5</sub> to C<sub>15</sub> range, said metathesis process including the step of subjecting a Fischer-Tropsch olefin feedstock in the C<sub>5</sub> to C<sub>15</sub> range to metathesis reaction conditions, said olefin feedstock including mono-methyl branched olefins.
2. The high temperature metathesis process as claimed in claim 1, wherein said process is carried out at a temperature of between 300°C to 600°C.
3. The high temperature metathesis process as claimed in claim 1, wherein said process is carried out at a temperature of between 450°C and 550°C.
4. The high temperature metathesis process as claimed in any one of claims 1 to 3, wherein said process is carried out at a pressure of between 1 and 30 bar.
5. The high temperature metathesis process as claimed in any one of claims 1 to 4, wherein said process is carried out in the presence of a tungsten or molybdenum based catalyst.

6. The high temperature metathesis process as claimed in any one of claims 1 to 4, wherein said process is carried out in the presence of a  $\text{WO}_3$  or  $\text{MoO}_3$  catalyst.

5 7. The high temperature metathesis process as claimed in any one of the preceding claims, wherein said Fischer-Tropsch olefinic feedstock in the  $\text{C}_5$  to  $\text{C}_{15}$  range includes at least linear alpha olefins and mono-methyl branched olefins.

10 8. The high temperature metathesis process as claimed in any one of the preceding claims, wherein said Fischer-Tropsch olefinic feedstock includes one or more olefins selected from the  $\text{C}_5$  to  $\text{C}_9$  range.

15 9. The high temperature metathesis process as claimed in any one of the preceding claims, wherein the product of the high temperature metathesis process includes one or more mono-methyl branched olefins in the  $\text{C}_9$  to  $\text{C}_{18}$  range.

20 10. The high temperature metathesis process as claimed in any one of the preceding claims, wherein the product of the high temperature metathesis process includes one or more linear olefins in the  $\text{C}_9$  to  $\text{C}_{18}$  range.

11. The high temperature metathesis process as claimed in any one of the preceding claims, wherein the olefins of the product are internal olefins.

12. The high temperature metathesis process as claimed in any one of the preceding claims, wherein the product of the high temperature metathesis process is used in the production of alkyl benzene, plasticizers, detergents, and/or drilling fluids, having both a linear fraction and a branched  
5 fraction.

13. The high temperature metathesis process as claimed in claim 12, wherein the branched fraction is mono-methyl branched.

10 14. The high temperature metathesis process as claimed in claim 13, wherein the branched fraction includes di-methyl, and/or ethyl branching.

15 15. A high temperature metathesis process for the metathesis of olefins in the C<sub>5</sub> to C<sub>15</sub> range, said metathesis process including the step of subjecting an olefinic feedstock in the C<sub>5</sub> to C<sub>15</sub> range to metathesis reaction conditions, the process including the recycling of a part of the product of the metathesis reaction to the reaction to increase the selectivity for a desired product range.

20 16. A high temperature metathesis process as claimed in claim 15, wherein the olefinic feedstock is a Fischer-Tropsch olefinic feedstock including mono-methyl branched olefins.

17. A high temperature metathesis process as claimed in claim 15 or claim 16, wherein the olefinic feedstock includes one or more olefins in the C<sub>5</sub> to C<sub>9</sub> range.

5 18. A high temperature metathesis process as claimed in claim 15, wherein the desired product range includes olefins in the C<sub>9</sub> to C<sub>18</sub> range.

19. A high temperature metathesis process as claimed in claim 18 wherein the process includes a separation stage wherein a recycle fraction in  
10 the C<sub>5</sub> to C<sub>8</sub> range is separated from the product and recycled to the reaction.

20. A high temperature metathesis process as claimed in claim 19, wherein the quantity of recycle in the feedstock is selected to provide a C<sub>9</sub> and higher selectivity of above 50%.

15

21. A high temperature metathesis process as claimed in claim 19 or claim 20, wherein the recycle makes up between 20% and 80% of the reaction feedstock.

20 22. A high temperature metathesis process as claimed in claim 21, wherein the recycle makes up between about a third and three quarters of the reaction feedstock.

23. A high temperature metathesis process as claimed in any one of claim 18 to 22, wherein the total yield of high temperature metathesis process product in the C<sub>9</sub> to C<sub>18</sub> range is above 40%.

5           24. A high temperature metathesis process as claimed in any one of claim 18 to 22, wherein the total yield of high temperature metathesis process product in the C<sub>9</sub> to C<sub>18</sub> range is above 50%.

25. A high temperature metathesis process as claimed in any one of  
10       claims 15 to 24, wherein the total feedstock conversion is in the range of 60% to 90%.

26. A high temperature metathesis process as claimed in claim 25,  
wherein the total feedstock conversion is about 80%.

15           27. A high temperature metathesis process as claimed in any one of claims 15 to 26, wherein the ratio of linear to branched high temperature metathesis process products is greater than 1:1.

20           28. A high temperature metathesis process as claimed in any one of claims 15 to 27, wherein the ratio of linear to branched high temperature metathesis process products is greater than 2:1.

29. A high temperature metathesis process as claimed in any one of claims 15 to 28, wherein the ratio of linear to branched high temperature metathesis process products is about 3:1.

5 30. A high temperature metathesis process as claimed in any one of claims 15 to 29, wherein the branching of the high temperature metathesis process products is predominantly mono-methyl branching.

31. A high temperature metathesis process as claimed in any one of  
10 claims 15 to 30, wherein the branching of the high temperature metathesis process products includes some di-methyl and/or ethyl branching.

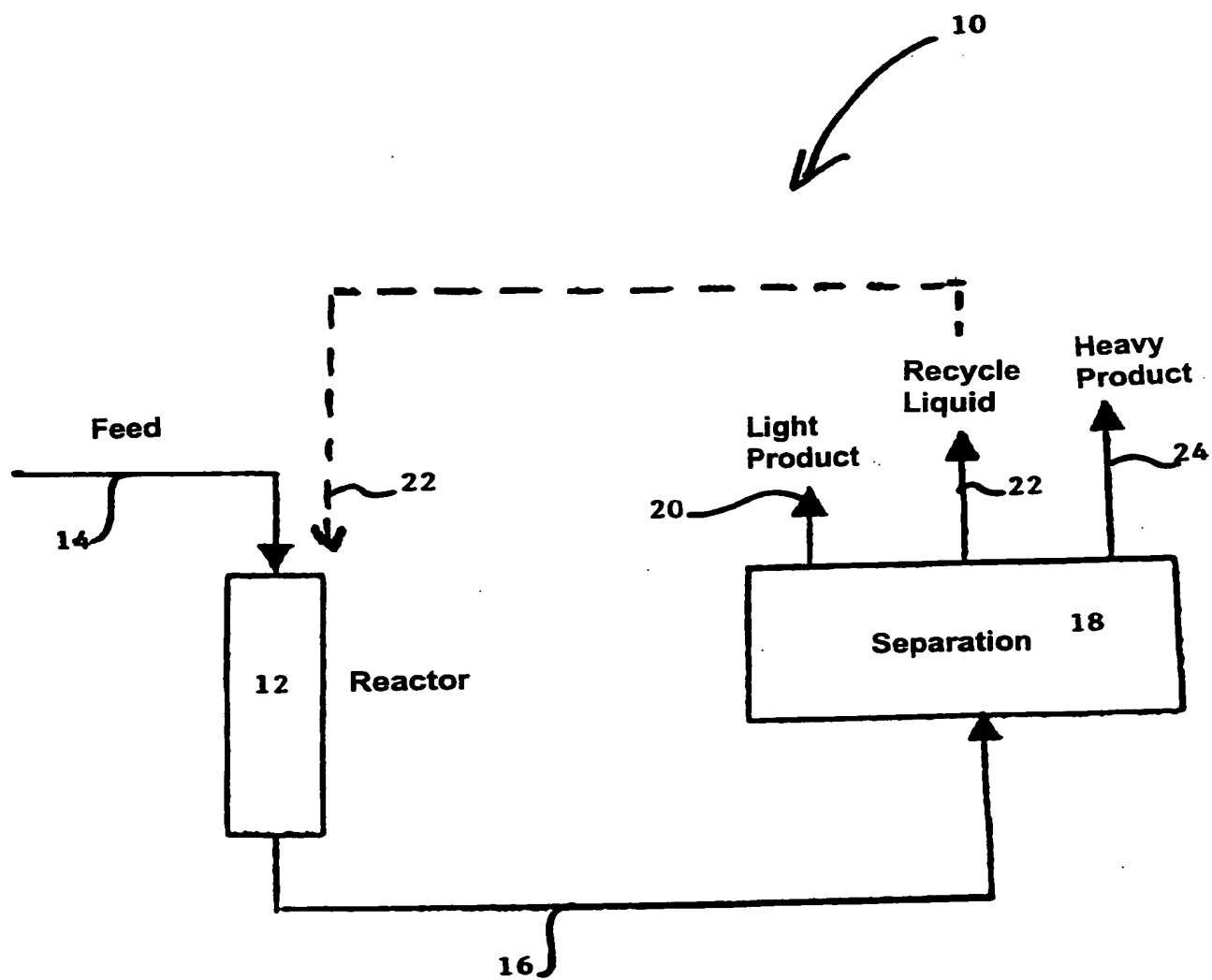
32. A high temperature metathesis process as claimed in any one of claims 15 to 31, wherein the products of the high temperature metathesis  
15 process are used in the production of alkyl benzene, plasticizers, detergents, and/or drilling fluids, having both a linear fraction and a branched fraction with the ratio of linear to branched fractions being related to the ratio of linear to branched high temperature metathesis process products used in their production.

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33. A high temperature metathesis process substantially as herein described and illustrated.

34. A new high temperature metathesis process substantially as  
25 herein described.

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## INTERNATIONAL SEARCH REPORT

International Application No

PCT/ZA 00/00120

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 C07C6/04

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	R. L. BANKS: "Catalytic Olefin Disproportionation" FORTSCHRITTE DER CHEMISCHEN FORSCHUNG - TOPICS IN CURRENT CHEMISTRY, vol. 25, 1972, pages 40-69, XP000953147 Berlin table 1	1-34
X	EP 0 538 750 A (MARUZEN PETROCHEMICAL CO) 28 April 1993 (1993-04-28) claims	1-34
X	EP 0 056 013 A (BP CHEMICALS ) 14 July 1982 (1982-07-14) claims	1-34
	— — — — — -/-	

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

26 October 2000

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# INTERNATIONAL SEARCH REPORT

tr. national application No

PCT/ZA 00/00120

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Information on patent family members

International application No

PCT/ZA 00/00120

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